THE REDUCTION OF MIXED HINDERED BENZILS

BY

PAUL EDWIN HOCH

A. B., Ohio Wesleyan University, 1942

M. S., Syracuse University, 1944

AN ABSTRACT OF A THESIS

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN CHEMISTRY
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Introduction

It has been previously noted that the reduction of mesityl phenyl diketone (1) and phenyl triisopropylphenyl diketone (2) with phosphorus and iodine resulted in the formation of phenyl 2,4,6-trimethylbenzyl ketone and phenyl 2,4,6-triisopropylbenzyl ketone in practically quantitative yields. The present work was undertaken to extend the hydrogen iodide reduction to other mixed hindered benzils with the view of determining the generality of this apparently anomalous reduction and, if possible, uncover factors which might influence it.

Discussion and Results

The benzils 4-methoxy-2,6-dimethylphenyl phenyl diketone (I), 2,4,6-triethylphenyl phenyl diketone (II), bromomesityl phenyl diketone (III), duryl phenyl diketone (IV) and isodurylphenyl diketone (V) were synthesized. The first three benzils (I, II, III) had not been prepared previously. All of the benzils but I were prepared by condensing phenylacetyl chloride with the substituted benzene compound in the presence of aluminum chloride and then oxidizing the desoxybenzoin thus formed with selenium dioxide to the benzil. Compound I was prepared by condensing phenylacetyl chloride with 4-methoxy-2,6-dimethylphenylmagnesium bromide and then oxidizing the desoxybenzoin with selenium dioxide.

The isomeric desoxybenzoins for each of the benzils but I were synthesized by allowing the substituted phenylacetyl chlorides to condense with diphenylcadmium. These were phenyl 2,4,6-triethylbenzyl ketone (VI), phenyl bromo-2,4,6-trimethylbenzyl ketone (VII), phenyl 2,3,5,6-tetramethyl-

benzyl ketone (VIII) and phenyl, 2,4,5,6-tetramethylbenzyl ketone (IX). Various attempts to prepare 4-methoxy-2,6-dimethylphenylacetyl chloride met with failure. The compound 4-methoxy-2,6-dimethylacetophenone was prepared but its synthesis could not be repeated. All of the desoxybenzoins prepared in the condensation with diphenylcadmium were new compounds and were characterized through the formation of their oximes.

The benzils II and IV upon reduction with zinc and acetic acid gave rather high yields, in each case, of compounds whose physical properties differed from those of either isomeric desoxybenzoin and whose analysis seemed to indicate that they could not be benzoins, stilbenes or glycols. The structures were not determined. Benzil V in a similar reduction gave the desoxybenzoin IX.

The reduction of the benzils with hydrogen iodide solution (Sp. Gr. 1.5, 47 per cent) in glacial acetic acid gave in practically quantitative yields the corresponding desoxybenzoins (VI, VII, VIII, IX). No other product was isolated. The oximes of the synthetic product and the reduction product were prepared in each case and their physical properties were also identical.

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VITA

The writer was born on November 6, 1920, in Philadelphia, Pennsylvania. He received his elementary education in the Philadelphia grammar schools and was graduated from Northeast High School, Philadelphia, in 1938. He entered Ohio Wesleyan University in September, 1938, and was graduated in June, 1942, with the degree of Bachelor of Arts. In September of the same year he entered the graduate School of Syracuse University, Syracuse, New York, from which he received the degree of Master of Science in May, 1944. In June he accepted a position of research assistant in the department of biochemistry at the University of Rochester, Rochester, New York, in connection with the Manhattan project, remaining there for one year. In September, 1945, he entered the University of Illinois Graduate School and held teaching assistantships from September, 1945, to June, 1946, and from September, 1947, to June, 1948. He held a University Fellowship from September, 1946, to June, 1947.

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